REDUCED GRAVITY PROCESSING OF HOMOGENIZED IMMISCIBLE METAL ALLOYS

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ABSTRACT

Reduced gravity material experiments to process and prepare unique metal alloy systems from normally immiscible liquid phase melts are described. The study of this previously unclassified group of materials is considered from several aspects. The effects of low gravity environment on the observed immiscibility limits of two phase liquid combinations are considered. Included are discussions of homogenized alloy processing covering production of materials with unique physical and electrical properties, consideration of basic solidification processes, and the potential application of homogenized alloys in the preparation of composite materials.

Potential experiment performance limitations, requirements and interface criteria are identified. These considerations will include both phenomenological materials behavior and the practical experiment software, hardware and astronaut interfaces. Requirements for experiment development and pre and post orbital test are also considered.

INTRODUCTION

The logical starting point in the study and development of any alloy system is the establishment and utilization of the equilibrium phase diagram. Excluding the high temperature metastable phases, most binary and pseudobinary systems can be represented schematically by three general types of phase diagrams: complete solid solubility, Figure 1; partial solid solubility, Figure 2; and formation of an intermediate

phase, Figure 3. The high temperature metastable phases, often used in specialized alloys, are usually achieved by cooling the alloy at a high enough rate to retain the metastable phase at lower temperatures, thus allowing subsequent heat treatment to modify the alloy and achieve the desired physical properties. Some of these techniques, and their potential applicability to these experiments will be described later.

Almost no attention has been given to the study and development of alloys based upon components which exhibit a liquid phase immiscibility. This is directly a reflection of the inability to form alloys from these systems. Figure 4 illustrates a typical two component system which exhibits a liquid phase miscibility gap, and Table 1 is a partial list of such binary systems showing liquid phase immiscibility. The phase line separating the homogeneous single liquid from the two phase liquid region is defined as the consulate temperature line and indicates the variation of composition with temperature. Above the consulate temperature line, T_c, the liquid phase consists of a single homogeneous solution of components A and B. The function W_a, "Work of adhesion" is defined as $W_a=\sigma A+\sigma B-\sigma AB$ (reference 1) where σ_A is the surface tension of liquid A, σ_B is the surface tension of liquid B, and σ_{AB} is the interfacial tension between the mutually saturated liquids A and B. This function is used in an attempt to define the structure of phase boundries. If W_a is large, σ_{AB} is small and the liquids are miscible. For small values of W_a, σ_{AB} is large and the liquids are immiscible. Since the surface tension of a pure liquid is a function of the temperature, and decreases with increase in temperature, then at some elevated temperature, the surface tensions of the two components will become approximately equal and the liquids will be miscible. For a number of actual systems, however, this temperature is sufficiently high such that one (or both) of the components have an appreciable vapor pressure which can lead to compositional variations or void formation in the alloy after solidification.

Conversely, alloy compositions having a consulate temperature in the liquid state with little or no vapor present will still segregate into two immiscible liquids as the melt is cooled. Thus in both cases, the alloy composition will traverse the immiscibility region during cooling. Further lowering of the temperature produces a liquid-solid mixture and ultimately a complete solid mixture of saturated components A and B. Due to any density difference between A and B, separation of phases of the liquid mixture is enhanced, and the solid mixture is thus segregated and of little value as an alloy. The major effects which dominate the solidification of immiscible liquid mixtures of this type are the surface tension and interfacial energy, and the gravitational separation of phases due to density differences. If these interactions could be modified, or sufficiently reduced, a new class of alloys could potentially be produced.

This can be demonstrated by examination of the Bond number for two immiscible liquids, obtained by a variation of the equations derived by Reynolds and Satterlee (reference 2). The Bond number compares the relative magnitudes of gravitational and capillary or surface tension forces, and is used as the parameter for delineating capillary-dominating or gravity dominating hydrostatics. For two immiscible fluids, the Bond number Bo approximates $Bo \simeq \frac{(\rho_A - \rho_B)\, r^2\, g}{2\, \sigma_{AB}}$

where: ρ = density of liquid A or B
r = radius of curvature between liquid A and liquid B
g = local acceleration in the gravitational field
σ_{AB} = interfacial tension between liquid A and liquid B

For values of Bo greater than 1, the gravitational force predominates, and for Bo less than 1, the capillary (or surface tension) forces predominate. Thus in a near zero gravity environment, the Bond number is less than one, and the system will be dominated by surface energy considerations. Depending upon the kinetics of the surface driving force to cause phase separation, it may be possible in a variety of immiscible alloy systems to produce homogenized alloys from the melt.

REDUCED GRAVITY PROCESSING OF HOMOGENIZED ALLOYS

The previous discussion dealt with equilibrium phase diagrams as measured in the earth's gravitational field. In the absence of the gravitational field, the phase diagrams possessing a liquid miscibility gap may change in that the position of the upper consulate line and the position of the solvous lines are sensitive to gravitational effects. The change in head pressure due to the near zero gravity conditions may effect the consulate temperature (reference 3), thus the original assumption that the surface tension forces will predominate as the driving force for phase separation appears to be valid. As the melt traverses the immiscibility region, appearance of the two components will occur, and the resultant surface tension dominated two phase liquid may take the form of a continuum liquid of the component having the lower surface tension with the other component finely dispersed throughout. For the melt to be stable in this region, the dispersed phase must be finely divided so that droplet growth will not occur (reference 4). Thus the melt should be in the form of an emulsion, and subsequent cooling will result in a fine grain homogenized alloy which may be crystalline or amorphous. If the alloy processing is initiated within the immiscibility region, rather than above the consulate line, then the requirement for homogenization in the solid phase region is that the melted component having the highest surface tension must be dispersed throughout the remaining component liquid phase in the form of finely divided liquid

droplets. With the assumption that these homogenized alloys are feasible to produce in a near-zero gravity environment, such alloys may offer a large area of potential usefulness in terms of their unique behavior, as discussed by the following examples.

Potential Extrinsic Semiconductor Alloy

Gallium arsenide, produced on earth, is a III-V compound semiconductor. It is finding usage as light emitting diodes, and is being developed for solid state microwave sources such as Gunn effect avalanche diodes or LSA (limited space charge accumulation) devices. The system gallium bismuth exhibits a liquid miscibility gap, and homogeneous alloys of these elements cannot be produced on earth. Since bismuth is in the same period as arsenic, a homogenized alloy of GaBi might exhibit extrinsic compound semiconducting qualities similar to gallium arsenide if it could be prepared in a manner to promote compound formation. An example of immiscible liquids which result in intermetallic compound formation at lower temperatures is found in the iron-tin system; it may therefore be possible to process an immiscible combination such as gallium and bismuth into atomically homogenized alloys, thereby promoting the interatomic bonding exhibited by the III-V semiconductor compound class.

Solid Lubricants

Copper-lead alloys have become commercially important as aircraft and automotive bearing materials. Although the copper-lead system has a liquid immiscibility gap, alloys of copper and lead containing up to about 30 weight percent lead can be produced without crossing the region of temperature and composition where the phase immiscibility occurs. The lubricating qualities of these alloys, however, increases with the lead content and therefore alloy compositions with a lead concentration of greater than 30 weight percent may be quite important. In the near-zero gravity environment, homogenized alloys containing almost any concentration of lead should be possible to be produced.

Directionally Solidified Composites

Directionally solidified composites as manufactured on earth are actually a binary eutectic reaction involving the transformation of a single liquid phase into two solid phases at a constant temperature. The reaction is invarient because it occurs in a system only when each of the three phases has a specific composition and at only one temperature. Thus, the "classical" type of directionally solidified eutectic composites would not benefit from a near-zero g environment. However, if one utilizes the homogeneous alloy concept, and maintained a unidirectional thermal gradient during solidification, the system is no longer invarient and the process can occur over a range of compositions within the immiscible region of the system. An example would

be the iron-lead system. If the molten iron-lead mixture is allowed to directionally solidify, it may be possible to produce single crystal fibers of iron directionally solidified in lead. Such a composite should have unique magnetic properties, as is the case with the directionally solidified Fe-FeS eutectic composite. Additionally, since the compositional range of the system can be varied, it should be possible to produce composite material having an extremely uniform microstructure phase spacing and alloy compositions which are not possible with eutectic alloy systems.

Alloys of Metals With Other Non-metallic Species

The homogenized alloy process is not necessarily limited to all metal systems. Any binary or pseudobinary system which exhibit a liquid miscibility gap should be capable of forming a homogenized alloy. Thus, mixtures of metals with metal oxides, carbides, nitrides, etc. are potential candidates for the homogenized alloy concept. Such alloys have the potential of producing unique cermet-like materials with structural and electronic applications.

In summary, the concept of homogenized alloys provides a basis for not only creating potentially unique materials, but will also contribute to the basic general understanding of gravitation effects on both liquid and solid alloy phases.

EXPERIMENTAL CRITERIA

The potential opportunity and possible types of homogenized alloys that may be processed in space in a near zero gravity environment has been outlined in the previous discussions. While these suggestions provide a basis for optimism in ultimately developing rewarding achievements, it is clear that a carefully designed experimental program to explore and develop these space manufacturing experiments will be required. Since the Orbital Workship is a closed ecological environment, and many types of experiments are planned, consideration of the interactions of the proposed homogenized alloy processing experiments with respect to the other experiments and the Orbital Workshop itself is necessary. These considerations consist of:

- Experiment Definition and Development
- Logistics Support Requirements for the Experiment Implementation
- Manned Interfaces

Experiment Definition and Development

This phase of the experimental criteria will consist of preorbital tests, astronaut interface considerations, and post orbital tests.

The preorbital tests should include a quantitative examination of the role of gravity (reduced gravity) on the phenomenological behavior of materials in the liquid state, and experimental attempts to produce small samples of homogenized alloys. The examination of the role of gravity should be based on both theoretical considerations, and modeling experiments with pairs of fluids having varying degrees of immiscibility and density gradients with respect to one another. In this manner, the interactions of density, surface tension and gravity can be estimated and correlated to the actual processing procedures necessary for the orbital experiments.

The preorbital experimental attempts to produce homogenized alloys should utilize the present procedures for obtaining metastable phases of alloys: rapid quenching from the liquid state ("splat cooling") (reference 5), and plasma-arc spraying or codeposition from the vapor phase onto a cooled substrate (reference 6). The splat cooling technique, particularly the levitation melt-shock tube ejection apparatus (reference 7), appears to be the most logical experimental method, since cooling rates on the order of 10^6°C/sec from the liquid to the solid state are achievable by this technique, thereby minimizing gravitational interactions during the liquid-solid transition. Although these methods produce relatively small samples, preliminary information can be obtained from examination of the types of materials likely to be obtained from the space manufacturing processes.

Consideration of the astronaut interface includes both the degree of involvement of the astronaut during the experiment, and the amount of subjective and/or objective judgment necessary for the astronaut to conclude if the experiment was a success or should be repeated, either under the same conditions or by varying experimental parameters. The interface should be minimal in all respects, in that the preorbital tests should delineate the processing parameters (temperatures, cooling rates, etc.), and the actual astronaut participation during the experiment be compatible with the other experiments on board, i.e., about the same involvement as would be required to cast a sphere or produce single crystals or glassy melts.

The post orbital alloy evaluation tests would be carried out on earth, and would consist of those measurements germane to the homogenized alloy produced: comprehensive metallurgical examination coupled with more detailed tests such as physical or electrical measurements. The results of these tests would then be correlated with the preorbital tests and the observations of the astronaut, and an evaluation of the feasibility of further homogenized alloy processing in space could then be carried out.

Logistics Support Requirements for the Experiment Implementation

The primary consideration of the logistics support requirements are that they are compatible with other processing experiments on board the Orbital Workshop. The compatibility requirements are power, thermal-temperature considerations, volume-weight considerations, and commonality of the processing hardware.

The basic process requirements for production of homogenized alloys are that the binary mixture be heated into the liquid state, held for a period of time at temperature, and then cooled to the solid state at some rate of cooling. The ancillary requirements are position control, thermal transfer or heating or cooling from the melt, and atmospheric control within the basic heating facility.

All of these requirements are common to the processing experiments which involve bulk melting of materials. The power requirement is dependent upon the sensible heat required to raise the materials to the melting point(s), the latent heats of fusion, and the excess energy to bring the melt to the proper liquidus temperature. Since relatively small quantities (0.1 to 1.0 kg) of bulk homogenized alloy, returned to earth, would be sufficient for laboratory examination and correlation of previous preorbital investigations, then the total logistics support requirements for the space manufacturing experiment package for processing homogenized alloys could be modeled to be compatible with the facility designed for the other experiments involving melting and/or casting processes. Assuming that the original processing experiments were successful, these same requirements would hold for successively larger amounts of homogenized alloys produced in larger Orbital Workshop space stations scheduled for future flights.

One exception to the above discussion would be the production of directionally solidified composites of homogenized alloys. In this particular process experiment, there is a need for a directional thermal gradient and the potential need for controlled nucleation sites. Thus, while the main logistics support is similar for the other processes, additional constraints are added in that the thermal control during solidification must be modified such that a thermal gradient force is imposed, and the solidification process will probably occur with the melt in contact with a solid support surface to provide directional nucleation growth sites for the homogenous composite. These facilities may be available for certain submerged liquid crystallization processes, and thus the commonality of the facilities is preserved. If such facilities are not available, the preorbital tests of nucleation processes as demonstrated by Lindé (reference 8) and Duwez, et al (reference 9) should give an indication of the facilities and process conditions necessary for combinations of these experiments in future space flights.

Manned Interfaces

This aspect of the space manufacturing of homogenized alloys is based upon the evaluation of the design of the equipment and procedures to support the astronaut worker in terms of human factors requirements and safety.

The human factors requirements for the process should be evaluated in terms of the design of equipment and procedures. Weight, complexity, and development status of such support equipment should be evaluated against frequency of usage and operating feasibility. Since a number of the proposed space manufacturing processes utilize similar facilities, the equipment must be based on standardization and generalization principles, with multipurpose tools and equipment favored over highly specialized ones, and provisions for restraint and locomotion during the processing periods to be given priority. Since a number of manufacturing processes have commonality, the design of such equipment and procedures should be compatible with the homogenized alloy process concept.

The safety aspect of space manufacturing processes must be evaluated in terms of safety to the astronaut under "worst case" conditions. This applies to all space manufacturing processes, and as such, each process must be analyzed and developed such that all equipment and processes will at all times be oriented toward maximum operating reliability and safety. Again, because of the commonality of the homogenized alloy process with other experiments, this consideration should be amenable to solution by evaluation of the various process requirements, and thus be a basis for evaluation and design of all equipment and facilities for these processes.

CONCLUSION

This paper has described the concept of processing homogenized alloy systems. An essential portion of this proposed program is to clearly identify the interactions between the materials experiment definition, the processing equipment/facility to implement the experiment, and the astronaut/worker requirements to obtain an experimental process result. Each of these interactions are summarized below.

Preliminary Experiment Definition

The preliminary experiment definition requires the utilization of preorbital tests in order to supplement theoretical considerations of near zero gravity processing of homogenized alloys. These evaluations include model immiscible liquid studies to evaluate density, surface tension, and thermodynamic limitations, in order to determine those which may be of value to pursue further in a near zero g environment and rapid quench cooling studies to establish physical properties of meritorious interest.

Examination of post orbital evaluation techniques are also necessary in order to determine if the near zero gravity processing has produced a unique and potentially valuable material. These evaluations will include both conventional and phenomenological behavioral characterizations to establish the uniqueness of the materials produced.

Implementation of the Processing Equipment and Facility

The development of the processing equipment and the facility must be coordinated with the overall experimental processing program in the Orbital Workshop. This development requires a close coupling of the materials science definition activity to the engineering constraints of equipment performance capabilities and process scheduling. If a homogenized alloy process, for example, requires a high temperature capability, then this requirement must be assessed against the total experimental processes to be performed, the available equipment, and the relative value of the potential returns to be gained by the experiment.

Astronaut/Worker Requirements

Pertinent consideration must be given to the astronaut skills and training requirements. Orbital process work schedules and real time evaluation criteria must be established. Overall care must be taken to assure safety in the materials selection, process schedules and facility design.

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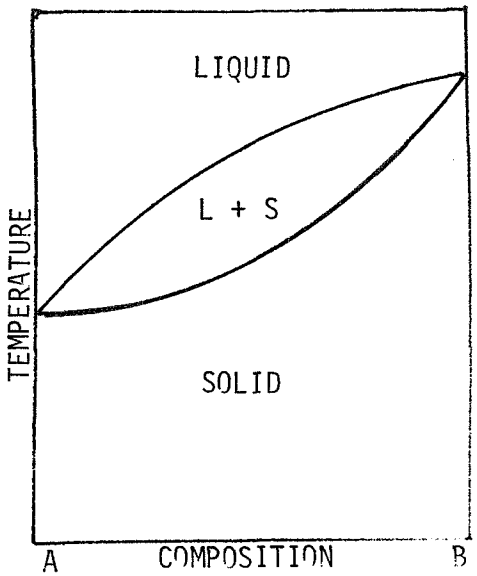

Figure 1
Complete Solid
Solubility

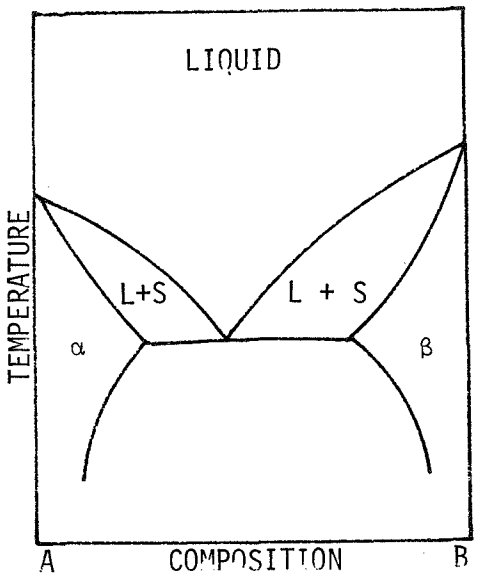

Figure 2
Partial Solid
Solubility

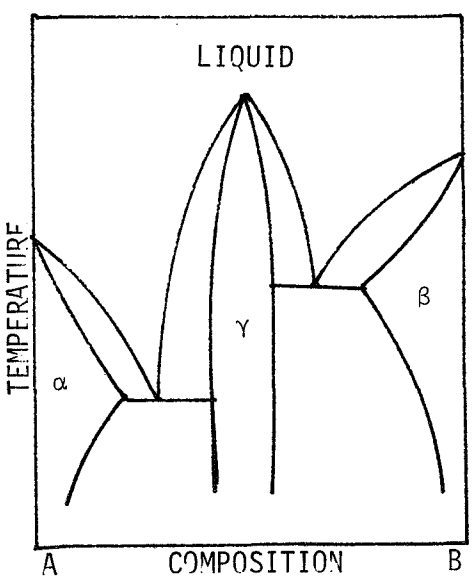

Figure 3
Presence of an
Intermediate Phase

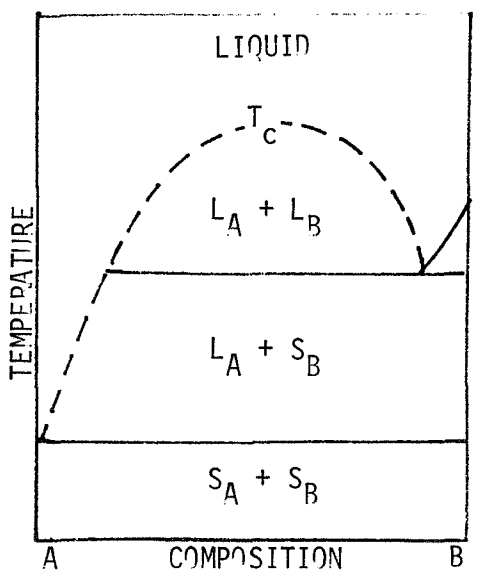

Figure 4
Presence of a Miscibility
Gap in the Liquid Phase

TABLE 1. Some Binary Alloy Systems Which Exhibit Liquid Phase Immiscibility

AgCr	BeGa	CoPb	GaHg	NaZn
AgMn	BeIn	CoSe	GaK	
AgNi	BeSn		GaPb	NiPb
AgRh		CrCu	GaTl	NiTl
AgS	BiCo	CrGd		
AgSe	BiCr	CrLa	InS	PbSi
AgTe	BiFe	CrPb		PbU
AgU	BiGa	CrS	KPb	PbZn
AgW	BiMn	CrSn	KZn	
	BiSi			PPt
AlBi	BiU	CuPb	LaMn	PTl
AlCd		CuS	LaPu	PSn
AlIn	CaCd	CuSe	LaV	
AlK	CaLa	CuTe		SSb
AlNa		CuTl	LiNa	SSn
AlPb	CbCe	CuU		STl
AlS	CbY	CuW	MgNa	
AlTl			MgPu	SeSn
	CdGa	ErV	MgU	SeSb
AsTl	CdK			SeTl
		FePb	MnPb	ThU
AuRh	CeMn	FeS	MnTl	ZnU
	CeU	FeSn	MnS	VY